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XXVI.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

I. ON CHLORPYROMUCIC ACIDS.*

BY HENRY B. HILL AND LOUIS L. JACKSON.

Presented May 28, 1889.

MANY years ago Malaguti † found that dry chlorine gas was quickly absorbed by ethyl pyromucate, and that a thick viscous liquid was formed, the composition of which showed that four atoms of chlorine had been taken up. The oil was carbonized on distillation, and yielded with potassic hydrate decomposition products which were not further studied. Although Schmelz and Beilstein ‡ later found that chlorine converted pyromucic acid in aqueous solution into mucochloric acid, and this reaction was afterwards further studied by Hill and Bennett,§ no further experiments, as far as we could learn, had ever been made with dry chlorine on pyromucic acid or its ethers. In 1884, after it had been shown by investigations carried on in this laboratory that substitution products could readily be formed from pyromucic acid by the action of dry bromine, Mr. J. N. Garratt, at that time an assistant in the laboratory, undertook the investigation of the action of dry chlorine under similar conditions. Although he succeeded in isolating a dichlorpyromucic acid melting at 167–168° in a state of purity, he found that the reaction differed in many respects from the corresponding reaction with bromine, and that the matter deserved a more careful study than he was then able to bestow upon it. Mr. Garratt relinquished his investigation of this subject in order to continue his studies in Zurich, and in the following winter

* A part of the work described in the following paper was presented in the form of a thesis to the Academic Council of Harvard University in May, 1888, by Louis L. Jackson, then candidate for the degree of Doctor of Philosophy.

† Ann. Chim. Phys., lxiv. 282; lxx. 371.

‡ Ann. Chem. u. Pharm., Suppl., iii. 276.

§ Berichte d. deutsch. chem. Gesellsch., xii. 655.

met with the fatal accident which so sadly ended his promising career.

The observations which already had been made interested us so much that in 1886 we undertook a more thorough study of the subject. We had already collected a great deal of material which we did not think it necessary to publish in a preliminary form, when Denaro * published in the *Gazzetta Chimica* a brief notice of a dichlorpyromucic acid melting at 167–168°, which was evidently identical with that prepared by Garratt. The paper contained a description of the acid and two of its salts, but the analyses of the latter did not agree with those which we had already obtained, and moreover contained such serious misprints or arithmetical errors, or both, as to be wholly without value. In consequence of the appearance of that paper, we thought it best to publish a preliminary account † of our work, so far as that one acid was concerned, more especially since our study of it was then essentially completed.

In repeating the experiments of Garratt, we had no difficulty in isolating the dichlorpyromucic acid which he had prepared, but we found that the reaction was still more complex than we had supposed. At ordinary temperatures chlorine was rapidly absorbed, but the pyromucic acid was soon so coated with the viscous addition product that a homogeneous product could not be obtained. On heating, the reaction could easily be pushed to the end, and the gain in weight closely corresponded with the addition of four atoms of chlorine. At the same time hydrochloric acid and carbonic dioxide were given off, and the resulting product contained a percentage of chlorine much larger than that demanded by any simple addition product. Under these circumstances it seemed advisable to return to the ethyl pyromucic tetrachloride of Malaguti, which, from his description and analyses, appeared to be homogeneous; and to take up the study of the more complex action of chlorine upon the acid itself after this investigation had made us better acquainted with some of the products likely to be formed. Although we were unable to prepare a perfectly homogeneous product by following the directions of Malaguti, we found no difficulty in so modifying the conditions that the resulting compound should give us pure $\beta\gamma$ dichlorpyromucic acid melting at 168–169°, δ chlorpyromucic acid melting at 176–177°, or trichlorpyromucic acid melting at 172–173°. The $\beta\delta$ dichlorpyromucic acid we were unable to prepare by direct substitution, or by saponification of ethyl pyromucic tetra-

* *Gazz. Chim.*, xvi. 333.
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† *Berichte d. deutsch. chem. Gesellsch.*, xx. 252.
21

chloride; but by distillation of ethyl pyromucic tetrachloride, of the tetrachloride of pyromucyl chloride, or of ethyl δ chlorpyromucic tetrachloride, the $\beta\delta$ dichlorpyromucic acid melting at $155-156^\circ$ may be obtained, and in the first two cases a third dichlorpyromucic acid melting at $197-198^\circ$ is also formed. By careful reduction of the $\beta\delta$ or the $\beta\gamma$ dichlorpyromucic acids, the β chlorpyromucic acid melting at $145-146^\circ$ is formed.

ETHYL PYROMUCIC TETRACHLORIDE.

The ethyl pyromucate which we have used in the course of our investigations we have made by warming a solution of pyromucic acid (3 parts) in absolute alcohol (5 parts) with concentrated sulphuric acid (3 parts acid, Sp. Gr. 1.84). After heating for four hours on the water bath, the mixture was allowed to cool, precipitated with water, and the ether washed with a dilute solution of sodic carbonate. The crude ether was then dried by exposure to the air and distilled. The yield of pure distilled ether which is thus obtained amounts to about 85 per cent of the weight of the acid taken. This is somewhat less than that which may be obtained by means of hydrochloric acid, but the method is much more expeditious and convenient.

When dry chlorine is passed over ethyl pyromucate we found that the ether was rapidly liquefied with the evolution of heat, and that the formation of the addition product proceeds as described by Malaguti until the ether has increased in weight very nearly the amount required by the addition of four atoms of chlorine. We soon found, however, that, no matter how carefully the chlorine was dried, hydrochloric acid escaped, showing the formation of a substitution product, and that the amount of hydrochloric acid formed depended largely upon the rapidity of the stream of chlorine and the consequent elevation of temperature. Even when the ether was carefully cooled to 0° during the whole of the treatment with chlorine, the formation of hydrochloric acid could not wholly be avoided. In this respect our experience agrees with that of Hill and Sanger,* who were unable to form the ethyl pyromucic tetrabromide without the simultaneous formation of substitution products. While the statements of Malaguti seemed to leave no room for doubt that the ethyl pyromucic tetrachloride was completely carbonized by heat, experiments made with bromine in this laboratory had shown that substitution products could readily be formed from the ethyl pyromucic tetrabromide by heat,

* These Proceedings, xxi. 155.

and it seemed to us hardly conceivable that complete carbonization should ensue. A preliminary trial showed so much less charring under ordinary pressure than we had anticipated, that we were encouraged to hope that the ethyl pyromucic tetrachloride itself might be distilled under diminished pressure without essential decomposition. Ethyl pyromucate was therefore carefully treated with chlorine at 0° until it ceased to gain in weight. Hydrochloric acid was given off in small quantity, and the total gain in weight was 94 per cent of the weight of ethyl pyromucate taken, instead of the theoretical gain of 101 per cent. The product was then fractionally distilled under a pressure of 15 mm. and showed its complex nature by the wide range of its boiling point, $104-160^{\circ}$. Above 160° there remained a residue which even under 15 mm. pressure could not be distilled without decomposition.

None of the fractions showed any tendency to solidify in a freezing mixture. After several distillations, it became evident that the greater portion boiled without essential decomposition between $150-160^{\circ}$, and that a smaller portion boiled below 110° .

In order to determine the nature of the several products, the following analyses were made. Each fraction was collected under 15 mm. pressure.

A. Boiling point $104-110^{\circ}$; weight = 2.6 gm.

0.2235 gm. substance gave 0.2139 gm. AgCl.

	Calculated for $C_6H_2ClO_3C_2H_5$.	Found.
Cl	20.34	23.63

B. Boiling point $145-150^{\circ}$; weight = 3.2 gm.

0.2334 gm. substance gave 0.4418 gm. Ag. Cl.

C. Boiling point $152-153^{\circ}$; weight = 7.7 gm.

I. 0.1678 gm. substance gave 0.3431 gm. AgCl.

II. 0.1415 gm. substance gave 0.2889 gm. AgCl.

D. Boiling point $153-157^{\circ}$; weight = 12.0 gm.

0.1502 gm. substance gave 0.3094 gm. AgCl.

	Calculated for $C_6H_5O_3C_2H_5Cl_4$.	B.	Found. C.		D.
			I.	II.	
Cl	50.36	46.77	50.55	50.49	50.97

From these analyses it was evident that the fraction C consisted of pure ethyl pyromucic tetrachloride; the fraction D contained a slight

admixture of a product containing a higher percentage of chlorine; the fraction A approached in composition the ethyl chlorpyromucate; while the fraction B was a mixture. In order to be quite sure of the correctness of our conclusions, we treated these successive fractions with an alcoholic solution of sodic hydrate, and obtained acids in each case confirming the results of our analyses. From fraction A we obtained an acid crystallizing from hot water in irregular leafy plates which melted at 176–177°. The physical properties and melting point were sufficient to identify this acid as the δ chlorpyromucic acid later described, and to prove that the lower boiling fraction consisted chiefly of ethyl δ chlorpyromucate. Fraction C yielded us without difficulty, and in nearly theoretical quantity, an acid which when recrystallized twice from benzol melted sharply at 168–169°, and in other respects proved to be identical with the $\beta\gamma$ dichlorpyromucic acid which we shall hereafter fully describe. The formation of this acid in nearly theoretical quantity and without recognizable admixture proves that the fraction C consisted of pure ethyl pyromucic tetrachloride. Fraction D yielded us a somewhat less pure $\beta\gamma$ dichlorpyromucic acid, as did also fraction B. In the latter case, however, we were able to isolate a small quantity of a sparingly soluble acid, crystallizing from water in minute needles which closely resembled trichlorpyromucic acid. It was therefore evident that the main product formed by the action of chlorine at 0° upon ethyl pyromucate was the tetrachloride and this might be distilled under diminished pressure without essential decomposition. At the same time, it was shown that substitution was effected even in the cold, and that the product contained ethyl δ chlorpyromucate and very possibly its tetrachloride.

δ CHLORPYROMUCIC ACID.

Since substitution had taken place at low temperatures, it seemed not unlikely that at 100° the substitution might be so rapid as to offer a convenient mode for the preparation of chlorpyromucic acids. Ethyl pyromucate when treated with bromine at 100° yields δ brompyromucic and $\beta\delta$ brompyromucic acids still more readily than pyromucic acid itself. We accordingly passed dry chlorine through ethyl pyromucate heated to 100°, but found that a higher temperature was necessary in order that substitution might promptly be effected. At 145° the action was sufficiently rapid, and the chlorine was passed through the melted ether at this temperature until a gain in weight was noted which corresponded to the substitution of one hydrogen atom by chlorine. The viscous liquid which was thus obtained was then slowly

added to an excess of a concentrated alcoholic solution of sodic hydrate, care being taken to avoid any great elevation of temperature. When the action was completed the sparingly soluble sodium salt was removed by filtration and dried. The alcoholic filtrate contained small quantities of this sodium salt in solution, and contained further a small amount of some volatile furfuran compound. We converted the excess of sodic hydrate into carbonate with carbonic dioxide, removed the sodic carbonate by filtration, and distilled the alcoholic filtrate. The distillate when mixed with water threw down a minute quantity of a colorless oil of peculiar aromatic odor, which we have as yet been unable to identify through lack of material. The small amount of sodium salt obtained from the alcoholic mother liquors was then added to the main portion. The sodium salt when dissolved in water and acidified with hydrochloric acid then yielded the crude δ chlorpyromucic acid, which not infrequently needed no other purification than recrystallization from benzol. If, however, the treatment with chlorine had been too long continued, or the action had taken place at too low a temperature, the product contained dichlorpyromucic and trichlorpyromucic acids which could not be removed by simple recrystallization. Whenever the crude acid failed on trial to crystallize from hot water in shining irregular plates, it was necessary to resort to chemical means for its purification. The acid was suspended in twenty times its weight of cold water, ammonia added in slight excess, and then baric chloride in quantity sufficient to precipitate the sparingly soluble barium salts of the admixed acids. After the separation of these salts is complete, the filtered solution gives on acidification an acid which crystallizes from water in leafy plates, and which may further be purified by recrystallization from benzol. The yield of chlorpyromucic acid thus obtained amounts to about 40 per cent of the weight of ether taken, or 38 per cent of the theoretical amount.

I. 0.2761 grm. substance gave 0.4145 grm. CO_2 and 0.0494 grm. H_2O .

II. 0.2667 grm. substance gave 0.2642 grm. AgCl .

III. 0.2990 grm. substance gave 0.2950 grm. AgCl .

	Calculated for $\text{C}_6\text{H}_3\text{ClO}_2$.	I.	Found.	
			II.	III.
C	40.96	40.94		
H	2.05	1.99		
Cl	24.23		24.49	24.39

The δ chlorpyromucic acid is readily soluble in hot water, sparingly in cold water, and crystallizes in large irregular leafy plates, which

closely resemble the corresponding bromine derivative. It dissolves readily in alcohol, ether, or hot benzol, but sparingly in cold benzol. The acid recrystallized from benzol melted at 176–177°, and a preparation made from the pure ethyl ether melted at the same point. Its solubility in cold water was determined according to the method of V. Meyer. A weighed portion of the solution saturated at 19°.5 was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

I. 37.8458 grm. solution saturated at 19°.5 gave 0.0833 grm. BaSO_4 .

II. 33.5216 grm. solution saturated at 19°.5 gave 0.0742 grm. BaSO_4 .

According to these determinations, the solution saturated at 19°.5 contained the following percentages of acid.

I.	II.
0.28	0.28

Baric δ Chlorpyromucate, $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. — The barium salt was prepared by boiling the acid with an excess of baric carbonate. The salt is quite readily soluble even in cold water, still more readily soluble in hot water, and separates from a hot concentrated solution in thin leafy plates, usually aggregated in globular form. The air-dried salt contains one molecule of water, which it loses rapidly at 100°.

I. 1.2193 grm. air-dried salt lost at 100° 0.0491 grm. H_2O .

II. 0.5932 grm. air-dried salt gave 0.3094 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.	Found.
		I. II.
H_2O	4.04	4.04
Ba	30.72	30.67

0.6909 grm. salt dried at 100° gave 0.3763 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ba	32.01	32.02

The solubility of the salt in cold water was determined according to the method of V. Meyer.

I. 9.3523 grm. solution saturated at 19°.5 gave 0.2932 grm. BaSO_4 .

II. 8.3395 grm. solution saturated at 19°.5 gave 0.2534 grm. BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt.

I.	II.
5.76	5.58

Calcic δ Chlorpyromucate, $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot 3 \text{H}_2\text{O}$. — The calcium salt was prepared by boiling the acid with an excess of calcic carbonate. It is readily soluble in hot water, rather sparingly soluble in cold water, and separates from a hot concentrated solution in clustered prisms with rectangular terminations. The air-dried salt contains three molecules of water. It effloresces slowly over sulphuric acid, and loses all its water readily at 100° .

I. 1.0814 grm. air-dried salt lost at 100° 0.1480 grm. H_2O .

II. 1.2247 grm. air-dried salt lost at 100° 0.1689 grm. H_2O .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot 3 \text{H}_2\text{O}$.	Found.	
		I.	II.
H_2O	14.03	13.70	13.79

I. 0.6236 grm. salt dried at 100° gave 0.2564 grm. CaSO_4 .

II. 0.5509 grm. salt dried at 100° gave 0.2244 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.	
		I.	II.
Ca	12.09	12.09	11.98

The solubility of the salt in cold water was determined according to the method of V. Meyer. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

I. 21.6494 grm. solution saturated at $19^\circ.5$ gave 0.1002 grm. CaSO_4 .

II. 17.7467 grm. solution saturated at $19^\circ.5$ gave 0.0809 grm. CaSO_4 .

The solution saturated at $19^\circ.5$ contained therefore the following percentages of anhydrous salt.

I.	II.
1.13	1.11

Potassic δ Chlorpyromucate, $\text{KC}_5\text{H}_2\text{ClO}_3$. — The potassium salt is readily soluble even in cold water, and separates from a hot concentrated solution on rapid cooling in fine branching needles; on slower cooling, in small thin oblique plates. The salt lost nothing in weight when dried at 120° , and analysis showed it to be anhydrous.

I. 0.6543 grm. salt dried at 120° gave 0.3100 grm. K_2SO_4 .

II. 0.6390 grm. salt dried at 120° gave 0.3018 grm. K_2SO_4 .

	Calculated for $\text{KC}_5\text{H}_2\text{ClO}_3$.	Found.	
		I.	II.
K	21.18	21.27	21.20

Argentie δ Chlorpyromucate, $\text{AgC}_5\text{H}_2\text{ClO}_3$. — The silver salt may best be prepared by precipitating a solution of the barium salt with argentic nitrate.

For analysis the precipitated salt was well washed, recrystallized from hot water, and dried *in vacuo* over sulphuric acid. It is sparingly soluble even in hot water, and separates from a hot concentrated solution in irregularly branching flattened needles.

I. 0.4843 grm. substance gave 0.2730 grm. AgCl.

II. 0.3948 grm. substance gave 0.2220 grm. AgCl.

Ag	Calculated for	Found.	
	$\text{AgC}_5\text{H}_2\text{ClO}_3$	I.	II.
	42.60	42.44	42.34

Ethyl δ Chlorpyromucate, $\text{C}_5\text{H}_2\text{ClO}_3\text{C}_2\text{H}_5$.—The ethyl ether was prepared by heating at 100° a solution of 5 parts of δ chlorpyromucic acid in 10 parts of absolute alcohol, with the addition of 5 parts of concentrated sulphuric acid (Sp. Gr. 1.84).

After heating for three hours, the ether was precipitated by the addition of water, washed first with dilute sodic carbonate, then with water, and finally dried with calcic chloride. The ether is a colorless heavy oil boiling at 216 – 218° (column completely in vapor) under a pressure of 76.8 mm., solidifying at 1 – 2° , and melting at the same point.

I. 0.2740 grm. substance gave 0.2219 grm. AgCl.

II. 0.2918 grm. substance gave 0.2402 grm. AgCl.

Cl	Calculated for	Found.	
	$\text{C}_5\text{H}_2\text{ClO}_3\text{C}_2\text{H}_5$	I.	II.
	20.34	20.02	20.35

δ Chlorpyromucamide, $\text{C}_5\text{H}_2\text{ClO}_2\text{NH}_2$.— δ chlorpyromucic ether is but slowly attacked by concentrated ammonia in the cold, and the amide may more readily be prepared from the acid chloride by means of solid ammonic carbonate. The amide is readily soluble in hot water, sparingly soluble in cold water and separates from a hot concentrated solution in fine branching needles, which melt at 154 – 155° .

For analysis, the amide was dried over sulphuric acid.

I. 0.1696 grm. substance gave 0.1677 grm. AgCl.

II. 0.2933 grm. substance gave 25.7 c.c. moist N at 25° and under a pressure of 764 mm.

Cl	Calculated for	Found.	
	$\text{C}_5\text{H}_2\text{ClO}_2\text{NH}_2$	I.	II.
	24.40	24.44	
N	9.62		9.82

Preparation I. was made from the ether, and II. from the acid chloride.

There seemed no room for doubt that the chlorpyromucic acid thus formed by the direct replacement of hydrogen by chlorine, like the δ brompyromucic acid obtained in a similar way, contained its chlorine in the δ position. We considered it necessary, however, to establish this point by direct experiment.

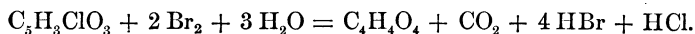
Action of Bromine and Water.

Although the action of bromine on δ brompyromucic acid suspended in water varied greatly with the conditions, Hill and Sanger* found that, when the oxidation was carefully conducted, fumaric acid alone was formed. We therefore suspended the δ chlorpyromucic acid in about twenty-five times its weight of water, and passed in bromine vapor slowly with a current of air. The acid gradually dissolved, and but little more than two molecules of bromine were needed to complete the oxidation. After standing for some time in the cold, the solution was evaporated to a small volume, and the crystalline acid which appeared as the solution cooled recrystallized from hot water. In this way we obtained a white crystalline acid which contained neither chlorine nor bromine, which was sparingly soluble in cold water, more readily in hot water, and which remained unchanged when heated to 200° . Although the acid was thus sufficiently characterized as fumaric acid, we further analyzed its silver salt.

0.4943 gram. substance dried at 120° gave 0.5591 gram. AgBr.

	Calculated for $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_4$	Found.
Ag	65.46	64.97

In the oxidation of the δ chlorpyromucic acid by bromine water, fumaric acid had therefore been formed according to the equation:



Action of Nitric Acid.

δ chlorpyromucic acid is not as readily attacked by nitric acid as the δ brompyromucic acid, and for its complete oxidation we found it necessary to heat one part of the acid with three parts of strong nitric acid (Sp. Gr. 1.42) diluted with twice its weight of water. After heating for three hours the oxidation was completed, and on evaporation fumaric acid was obtained, which was recognized by its sufficiently characteristic physical properties.

* These Proceedings, xxi. 144.

β CHLORPYROMUCIC ACID.

Hill and Sanger* found no difficulty in preparing β brompyromucic acid by the reduction of either of the two dibrompyromucic acids described by them. The corresponding dichlorpyromucic acids we found to be much more refractory, and we succeeded in preparing the β chlorpyromucic acid only after many unsuccessful attempts. The $\beta\gamma$ dichlorpyromucic acid, which was the more accessible, proved to be the more difficult of reduction, so that almost the whole of the material for this investigation was made from the $\beta\delta$ dichlorpyromucic acid. When zinc dust is added to a cold ammoniacal solution of this acid, no perceptible reaction takes place, and even after long standing no essential change can be detected. Even when the ammoniacal solution is boiled with a large excess of zinc dust the reduction is but slowly effected, and long continued heating is necessary to complete the reaction. We have found it advantageous to dissolve the acid in about twenty times its weight of dilute ammonic hydrate, to add an equal weight of zinc dust, and to boil for eight or ten hours, taking care to keep the solution strongly ammoniacal. The filtered solution is then cooled and acidified with dilute sulphuric acid, the acid which separates removed by filtration, the filtrate extracted with ether, and the residue left upon the evaporation of the ether added to the main product. The crude acid thus obtained melted at about 130° , and evidently contained unaltered $\beta\delta$ dichlorpyromucic acid. We therefore dissolved it in dilute ammonic hydrate, and added to the ammoniacal solution calcic chloride as long as a sparingly soluble calcium salt was promptly precipitated. The filtered solution then gave, when acidified with hydrochloric acid, a crystalline acid, which after recrystallization from hot water melted at $145-146^{\circ}$, and proved upon analysis to be a chlorpyromucic acid. From the sparingly soluble calcium salt, which had been removed by filtration, we obtained only unaltered $\beta\delta$ dichlorpyromucic acid, which in its turn was treated with zinc dust. In this way we found it possible to obtain from the $\beta\delta$ dichlorpyromucic acid at least 80 per cent of the theoretical amount of pure β chlorpyromucic acid. Zinc dust, even after long boiling, seems to have but little action upon $\beta\gamma$ dichlorpyromucic acid in ammoniacal solution, but sodium amalgam slowly reduces it at 100° . In order to effect complete reduction, it proved to be necessary to use a large excess of sodium in the form of a one per cent amalgam, and the reaction was then completed after heating for three hours on the water bath.

* These Proceedings, xxi. 147.

The acid obtained by acidification melted at 145–146°, contained the percentage of chlorine required by a chlorpyromucic acid, and appeared to be in all respects identical with the acid obtained from the $\beta\delta$ dichlorpyromucic acid. While the yield of pure acid was in this case but 50 per cent of the theoretical amount, it is possible that it might be somewhat increased by further experiments. From the third isomeric dichlorpyromucic acid, subsequently described, we have as yet been able to obtain no definite reduction product.

The β chlorpyromucic acid dried over sulphuric acid gave on analysis the following results:—

- I. 0.2710 grm. substance gave 0.4073 grm. CO_2 and 0.0513 grm. H_2O .
 II. 0.1385 grm. substance gave 0.1355 grm. AgCl .
 III. 0.1736 grm. substance gave 0.1692 grm. AgCl .

	Calculated for $\text{C}_8\text{H}_9\text{ClO}_3$.	I.	Found. II.	III.
C	40.96	40.99		
H	2.05	2.10		
Cl	24.23		24.18	24.10

Analysis III. was made with material prepared from the $\beta\gamma$ dichlorpyromucic acid.

β chlorpyromucic acid is readily soluble in hot water, sparingly soluble in cold water, and crystallizes from hot aqueous solution in thin irregular striated plates or flattened prisms. It is readily soluble in alcohol, ether, hot benzol or hot chloroform, and is but sparingly soluble in cold benzol or cold chloroform. When repeatedly crystallized from hot water it melted at 145–146°, and recrystallization from other solvents failed to raise this melting point.

In order to determine the solubility of the acid in cold water, a weighed quantity of a solution of the acid saturated at 19°.8 was boiled with baric carbonate, and the barium taken into solution precipitated as sulphate.

- I. 31.6300 grm. solution saturated at 19°.8 gave 0.2019 grm. BaSO_4 .
 II. 34.0328 grm. solution saturated at 19°.8 gave 0.2176 grm. BaSO_4 .

The solution saturated at 19°.8 therefore contained the following percentages of the acid:—

I.	II.
0.80	0.80

For the further characterization of the acid we prepared certain of its salts.

Baric β Chlorpyromucate, $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$. — The barium salt was prepared by boiling a solution of the acid with an excess of baric carbonate. The filtered solution was evaporated, and the salt which separated on cooling recrystallized from hot water. It proved to be readily soluble in hot water, more sparingly soluble in cold water, and crystallized in long obliquely terminated prisms, which contained one molecule of water. The salt is permanent in the air or over sulphuric acid, but loses its water readily at 100° .

I. 0.6092 gm. of the air-dried salt gave 0.3180 gm. BaSO_4 .

II. 1.3540 gm. of the air-dried salt lost at 100° 0.0576 gm. H_2O .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$.	I.	Found. II.
Ba	30.72	30.69	
H_2O	4.04		4.25

0.4749 gm. of the salt dried at 100° gave 0.2587 gm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ba	32.01	32.03

The solubility of the salt in cold water was determined in the usual way.

I. 10.2683 gm. solution saturated at $19^\circ.1$ gave 0.1149 gm. BaSO_4 .

II. 6.8737 gm. solution saturated at $19^\circ.1$ gave 0.0747 gm. BaSO_4 .

According to these determinations, the aqueous solution saturated at $19^\circ.1$ contained the following percentages of the anhydrous salt: —

I.	II.
2.06	2.00

Calcic β Chlorpyromucate, $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot 3 \text{H}_2\text{O}$. — This salt was prepared by neutralizing with calcic carbonate a boiling solution of the acid. If the solution thus obtained is evaporated upon the water bath clustered, pointed prisms of an anhydrous salt are formed when the solution becomes highly concentrated. By evaporation *in vacuo* over sulphuric acid at ordinary temperatures, tufts of fine branching prisms are obtained which contain three molecules of water. The latter salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 105° .

I. 0.4226 gm. of the air-dried salt gave 0.1490 gm. CaSO_4 .

II. 1.3627 gm. of the air-dried salt lost at 105° 0.1902 gm. H_2O .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2 \cdot 3 \text{H}_2\text{O}$.	I.	Found. II.
Ca	10.39	10.37	
H_2O	14.03		13.95

0.5160 grm. of the salt dried at 105° gave 0.2111 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ca	12.09	12.03

The pointed prisms obtained by evaporating the solution at 100° gave the following results.

0.4433 grm. of the air-dried salt gave 0.1796 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{H}_2\text{ClO}_3)_2$.	Found.
Ca	12.09	11.92

The solubility of the calcium salt in cold water was determined in the usual manner. The calcium was precipitated as oxalate, and converted into the sulphate before weighing.

I. 5.0960 grm. solution saturated at 19°.5 gave 0.0653 grm. CaSO_4 .

II. 5.8981 grm. solution saturated at 19°.5 gave 0.0752 grm. CaSO_4 .

According to these determinations, the aqueous solution saturated at 19°.5 contained the following percentages of the anhydrous salt: —

I.	II.
3.12	3.10

Ethyl β Chlorpyromucate, $\text{C}_5\text{H}_2\text{ClO}_3 \cdot \text{C}_2\text{H}_5$. — The ethyl ether was prepared by heating at 100° for four hours a mixture of 2 parts of the acid, 3 parts of absolute alcohol, and 2 parts of sulphuric acid (Sp.Gr. 1.84). On dilution with water the ether separated as an oil, which was thoroughly washed and dried over calcic chloride. It then distilled without essential decomposition at 217° (mercury column completely in vapor) under a pressure of 764 mm. The liquid distillate solidified on cooling, with the formation of concentrically grouped prisms, which, after repeated recrystallization by cooling the melted ether, showed the constant melting point of 29–30°.

0.1864 grm. of substance gave 0.1523 grm. AgCl .

	Calculated for $\text{C}_5\text{H}_2\text{ClO}_3 \cdot \text{C}_2\text{H}_5$.	Found.
Cl	20.34	20.19

Action of Nitric Acid.

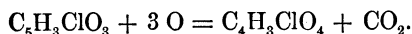
β chlorpyromucic acid is readily attacked by dilute nitric acid, but the oxidation is not smoothly effected, and the yield of chlorfumaric acid is comparatively small. The best results were obtained when the acid was boiled with 2 parts of nitric acid (Sp. Gr. 1.42) diluted with

5 parts of water. After the lapse of two hours, the action appeared to be completed, although a few drops of oil were still suspended in the clear solution. The products of the reaction were then extracted from the diluted solution with ether, the residue obtained by the evaporation of the ether pressed thoroughly with filter-paper and dried at 100°. The dry residue was then repeatedly washed with benzol in which chlorfumaric acid is but sparingly soluble. The product thus obtained was readily soluble in water, almost insoluble in benzol, melted at 188°, and contained the percentage of chlorine required by chlorfumaric acid.*

0.1089 grm. substance dried over H_2SO_4 gave 0.1027 grm. AgCl .

	Calculated for $\text{C}_4\text{H}_3\text{ClO}_4$.	Found.
Cl	23.59	23.31

The reaction may therefore be represented, in part at least, by the equation



Action of Bromine and Water.

Since β brompyromucic acid in aqueous solution is readily converted by an excess of bromine into mucobromic acid,† it seemed to us of interest to study the behavior of the β chlorpyromucic acid under the same conditions, since a product containing bromine and chlorine might then be formed. The acid was therefore suspended in five times its weight of water, and an excess of bromine at once added. After heating for a short time a clear nearly colorless solution was obtained, which was concentrated by evaporation on the water bath. On cooling, the solution deposited a crystalline acid which was readily soluble in hot water or hot benzol, and but sparingly soluble in these solvents in the cold. The acid recrystallized from water formed thin rhombic plates which melted at 120–121°, but this melting point could easily be raised to 121–122° by recrystallization from benzol.

An analysis of the substance dried over sulphuric acid showed that it was the mucochlorbromic acid whose formation we had been led to expect.

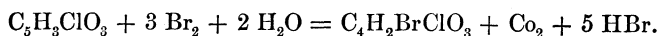
0.2871 grm. substance gave 0.4486 grm. $\text{AgCl} + \text{AgBr}$.

	Calculated for $\text{C}_4\text{H}_2\text{BrClO}_3$.	Found.
Br + Cl	54.11	54.45

* Kauder (Journ. f. prakt. Chem., [2], xxxi. 28) gives the melting point of chlorfumaric acid as 191°.

† These Proceedings, xxi. 152.

The reaction was then precisely analogous to that by means of which mucobromic acid was formed from β brompyromucic acid:



With the material which for the moment was at our disposal, we were unable to study the decomposition of the mucochlorbromic acid by alkalies. We shall hope in the future to prepare in this way a chlorbromacrylic acid, and compare it with the acid of the same composition already described by Mabery and Loyd.*

$\beta\gamma$ DICHLORPYROMUCIC ACID.

Hill and Sanger † had shown that in the decomposition of pyromucic tetrabromide or of ethyl pyromucic tetrabromide by alcoholic sodic hydrate, two isomeric dibrompyromucic acids are formed in not widely unequal quantities. There was, therefore, every reason to expect that two isomeric dichlorpyromucic acids could be found in the product formed in a similar way from ethyl pyromucic tetrachloride. Since we had found that a low temperature was essential to the preparation of a pure product, we allowed the ethyl pyromucate to absorb chlorine at 0° until a constant weight was reached, expelled the excess of chlorine by a current of dry air, and decomposed the product at once with an excess of an alcoholic solution of sodic hydrate. The best results were obtained when the tetrachloride was slowly added to a concentrated sodic hydrate solution, taking care to keep the mixture cold.

The sodium salts formed are sparingly soluble in alcohol, and after a short time can be removed by filtration. The alcoholic solution was freed from the excess of sodic hydrate by means of carbonic dioxide, and, after removing the sodic carbonate by filtration, distilled. The sodium salts left on distillation appeared to be identical with those already obtained and were therefore added to the main portion. The alcoholic distillate grew turbid when mixed with water, and gradually deposited a small quantity of a colorless oil which had a peculiar aromatic odor. The quantity of this oil was so small that no investigation of it has as yet been made.

The sodium salt which was obtained from the tetrachloride was dried, dissolved in hot water, and acidified with hydrochloric acid. In this way an acid was obtained which crystallized in finely felted needles which usually melted at 155° . After two recrystallizations from benzol the acid melted at $168\text{--}169^\circ$, and further recrystalliza-

* These Proceedings, xvi. 238.

† These Proceedings, xxi. 156.

tions failed to raise this melting point. Analysis showed this acid to be a dichlorpyromucic acid.

I. 0.4235 grm. substance gave 0.5135 grm. CO_2 and 0.0455 grm. H_2O .

II. 0.2332 grm. substance gave 0.3695 grm. AgCl .

III. 0.2195 grm. substance gave 0.3490 grm. AgCl .

	Calculated for $\text{C}_5\text{H}_2\text{Cl}_2\text{O}_3$.	I.	Found. II.	III.
C	33.15	33.07		
H	1.10	1.19		
Cl	39.22		39.16	39.31

The acid, which proved on subsequent investigation to be the $\beta\gamma$ dichlorpyromucic acid, is sparingly soluble in cold water, readily in hot, and crystallizes as the solution cools in finely felted needles. It is readily soluble in alcohol, ether, or in hot benzol; in cold benzol it is sparingly soluble and crystallizes from it in short prisms. In hot chloroform it is also readily soluble, sparingly soluble in the cold. The ready purification of this acid by recrystallization rendered it improbable that any sensible amount of an isomeric acid was formed with it. The most patient search has failed to show the formation of such a product in appreciable quantity, and from pure ethyl pyromucic tetrachloride almost pure $\beta\gamma$ dichlorpyromucic acid is obtained at once. The yield of pure acid ordinarily obtained from pyromucic ether is not wholly satisfactory, since it amounts to about 50 per cent of the weight of ether taken, or about 39 per cent of the theoretical amount.

The solubility of the acid in cold water we determined as usual. A weighed quantity of a solution of the acid saturated at 19.5° was boiled with baric carbonate and the barium dissolved precipitated by sulphuric acid.

I. 36.2505 grm. solution saturated at $19^\circ.5$ gave 0.0619 grm. BaSO_4 .

II. 35.6546 grm. solution saturated at $19^\circ.5$ gave 0.0615 grm. BaSO_4 .

According to these determinations, the solution saturated at $19^\circ.5$ contains the following percentages of acid: —

I.	II.
0.27	0.27

Baric $\beta\gamma$ Dichlorpyromucate, $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3) \cdot 3 \text{H}_2\text{O}$.* — The barium salt may be most conveniently prepared by precipitating a solution of the

* We have already referred to the brief description of the $\beta\gamma$ dichlorpyromucic acid published by Denaro in the *Gazzetta Chimica* (xvi. 333), and have asserted that the analyses of the two salts which he describes are not worthy of confidence. In support of our assertion we append his results in full, together

ammonium salt with baric chloride. It is rather sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in fine clustered needles which contain three molecules of water. The crystals are permanent in the air, but lose their water readily at 100°.

- I. 1.2048 grm. air-dried salt lost at 100° 0.1170 grm. H₂O.
 II. 1.2118 grm. air-dried salt lost at 100° 0.1132 grm. H₂O.
 III. 0.5694 grm. air-dried salt gave 0.2393 grm. BaSO₄.
 IV. 0.3783 grm. air-dried salt gave 0.1593 grm. BaSO₄.

	Calculated for Ba(C ₆ HCl ₂ O ₃) ₂ · 3 H ₂ O.	I.	II.	Found.	III.	IV.
H ₂ O	9.80	9.71	9.34			
Ba	24.86				24.71	24.76

- I. 0.4828 grm. salt dried at 100° gave 0.2250 grm. BaSO₄.
 II. 0.5540 grm. salt dried at 100° gave 0.2579 grm. BaSO₄.

	Calculated for Ba(C ₆ HCl ₂ O ₃) ₂ .	I.	II.	Found.
Ba	27.56	27.40	27.36	

The solubility of the salt in water at 19°.5 was determined according to the method of V. Meyer.

with the analytical data upon which they depend. The errors in the calculated percentages are corrected in parenthesis.

Barium salt:

0.4480 grm. of the salt lost at 110° 0.00204 grm. H₂O.

	Calculated for Ba(C ₆ HCl ₂ O ₃) ₂ · 3 H ₂ O.	Found.
H ₂ O	9.80	8.30 (0.445)

0.1939 grm. of the dry salt gave 0.0769 grm. BaSO₄.

	Calculated for Ba(C ₆ HCl ₂ O ₃) ₂ .	Found
Ba	23.54 (27.56)	23.32

Calcium salt:

0.6942 grm. of the salt lost at 110° 0.0300 grm. H₂O.

	Calculated for Ca(C ₆ HCl ₂ O ₃) ₂ · 3½ H ₂ O.	Found.
H ₂ O	13.60	14.45 (4.32)

0.3024 grm. of the salt gave 0.1072 grm. CaSO₄.

	Calculated for Ca(C ₆ HCl ₂ O ₃) ₂ .	Found.
Ca	10.00	10.42

These results can hardly be explained unless it is assumed that they contain both typographical and arithmetical errors. The two remaining analyses contained in Denaro's paper, two chlorine determinations in the free acid are correctly calculated, and agree well with the theory.

- I. 23.0222 grm. solution saturated at $19^{\circ}.5$ gave 0.0503 grm. BaSO_4 .
 II. 22.4890 grm. solution saturated at $19^{\circ}.5$ gave 0.0487 grm. BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt.

I.	II.
0.46	0.46

Calcic $\beta\gamma$ Dichlorpyromucate, $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$. — The calcium salt was prepared by boiling a solution of the acid with an excess of calcic carbonate. It is readily soluble in hot water, less soluble in cold, and crystallizes from a hot concentrated solution in long clustered needles which contain four molecules of water.

The crystallized salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water readily at 110° .

- I. 2.7640 grm. air-dried salt lost at 110° 0.4160 grm. H_2O .
 II. 3.1275 grm. air-dried salt lost at 113° 0.4707 grm. H_2O .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.	I.	II.
H_2O	15.26	15.05	15.05

- I. 0.6595 grm. salt dried at 110° gave 0.2227 grm. CaSO_4 .
 II. 0.7004 grm. salt dried at 113° gave 0.2366 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	I.	II.
Ca	10.00	9.93	9.94

The solubility of the salt in water at 19.5° was determined as usual. The calcium was precipitated as oxalate and the oxalate ignited with sulphuric acid.

- I. 22.8797 grm. solution saturated at $19^{\circ}.5$ gave 0.0944 grm. CaSO_4 .
 II. 21.5915 grm. solution saturated at $19^{\circ}.5$ gave 0.0891 grm. CaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of anhydrous salt:

I.	II.
1.21	1.21

Potassic $\beta\gamma$ Dichlorpyromucate, $\text{KC}_5\text{HCl}_2\text{O}_3$. — The potassium salt is readily soluble in hot water, but rather sparingly soluble in cold water, and separates from a hot concentrated solution in small prisms which are anhydrous.

- I. 0.6130 grm. substance dried at 120° gave 0.2435 grm. K_2SO_4 .
 II. 0.8200 grm. substance dried at 120° gave 0.3265 grm. K_2SO_4 .

	Calculated for $\text{KC}_5\text{HCl}_2\text{O}_3$.	I.	II.
K	17.84	17.83	17.87

Argentio $\beta\gamma$ Dichlorpyromucate, $\text{AgC}_5\text{HCl}_2\text{O}_3$. — If argentic nitrate is added to a cold aqueous solution of the acid, the silver salt is precipitated in the form of fine needles. For analysis we prepared the salt by precipitating a dilute neutral solution of the ammonium salt with argentic nitrate, and recrystallizing the precipitated salt from hot water. It is sparingly soluble even in hot water, and separates on cooling the hot saturated solution in fine needles.

- I. 0.3230 grm. substance dried over H_2SO_4 gave 0.1612 grm. AgCl .
 II. 0.2580 grm. substance dried over H_2SO_4 gave 0.1282 grm. AgCl .

	Calculated for $\text{AgC}_5\text{HCl}_2\text{O}_3$.	I.	Found. II.
Ag	37.50	37.57	37.41

Ethyl $\beta\gamma$ Dichlorpyromucate, $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$. — The ethyl ether was prepared by heating at 100° for three hours a mixture of 5 parts of acid, 8 parts of absolute alcohol, and 5 parts of concentrated sulphuric acid (Sp. Gr. 1.84). It was precipitated with water, washed with dilute sodic carbonate, and then with water. It is readily soluble in hot alcohol, more sparingly in cold, and crystallizes in large needles which melt at $63\text{--}64^\circ$.

- I. 0.2645 grm. substance dried over H_2SO_4 gave 0.3640 grm. AgCl .
 II. 0.1933 grm. substance dried over H_2SO_4 gave 0.2673 grm. AgCl .

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$.	I.	Found. II.
Cl	33.98	34.02	34.18

$\beta\gamma$ Dichlorpyrmucamide, $\text{C}_5\text{HCl}_2\text{O}_2\text{NH}_2$. — The ethyl ether of $\beta\gamma$ dichlorpyromucic acid is readily attacked by strong aqueous ammonia even in the cold, and in a short time is converted into the amide. The amide is sparingly soluble even in hot water, and crystallizes in long slender needles which melt at $176\text{--}177^\circ$.

0.4015 grm. substance dried over H_2SO_4 gave 28.5 c.c. moist N at 23° under a pressure of 767 mm.

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_2\text{NH}_2$.	Found.
N	7.78	8.03

The formation of but one dichlorpyromucic acid in the decomposition of the ethyl pyromucic tetrachloride by alkalies, while two isomeric acids are always obtained under the same circumstances from the corresponding bromine compound, made it impossible to predict its constitution from the method of formation. Still, its comparatively high melting point, its physical properties, and the ready solubility of

its calcium salt, in which it closely resembled the $\beta\gamma$ dibromopyromucic acid, gave fair ground for the conjecture that it had a similar structure. A study of its oxidation products showed that such was the case, since we easily obtained from it mucochloric and dichlormaleic acids.

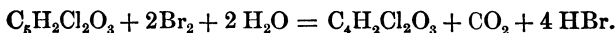
Action of Bromine and Water.

If bromine is added to $\beta\gamma$ dichlorpyromucic acid suspended in six or eight times its weight of cold water, oxidation rapidly ensues, with the escape of carbonic dioxide. A slight excess of bromine was added, and the reaction completed by the aid of heat. On cooling, the solution solidified with the separation of colorless crystals, which when recrystallized from water and finally from benzol melted at 124–125°, and had the characteristic form of mucochloric acid. Analysis also gave the proper percentage of chlorine.

- I. 0.2015 grm. substance dried over H_2SO_4 gave 0.3408 grm. AgCl .
 II. 0.2320 grm. substance dried over H_2SO_4 gave 0.3922 grm. AgCl .

	Calculated for $\text{C}_4\text{H}_2\text{Cl}_2\text{O}_3$.	Found.	
		I.	II.
Cl	42.01	41.81	41.79

In this case the reaction may be represented by the equation



Action of Nitric Acid.

Nitric acid acts but slowly upon the $\beta\gamma$ dichlorpyromucic acid, and for its complete oxidation we have found it necessary to take for one part of the acid 3 parts of concentrated nitric acid (Sp. Gr. 1.42) diluted with twice its weight of water. After boiling for five hours the action appeared to be complete, and as the clear solution deposited nothing on cooling we extracted it with ether. The ether left upon evaporation a colorless crystalline mass, which proved to be a mixture of two substances, one readily soluble, the other but sparingly soluble in cold water. The sparingly soluble substance when recrystallized from hot water was recognized by its crystalline form and by its melting point, 124–125°, as mucochloric acid. The acid, which was readily soluble in cold water, was neutralized with baric carbonate, the barium salt precipitated from its aqueous solution by alcohol, and the acid liberated from this purified barium salt again extracted with ether. The crystalline acid left by the evaporation of the ether was then dissolved in a small amount of water, and on standing well

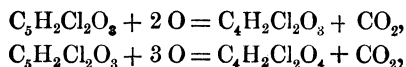
formed rhombic plates separated which were dried over sulphuric acid for analysis.

0.2233 grm. substance gave 0.3433 grm. AgCl.

	Calculated for $C_4H_2Cl_2O_4$.	Found.
Cl	38.38	38.01

The identity of this acid with dichlormaleic acid was further determined by the melting point of the anhydride prepared by sublimation, which we found to be $119-120^\circ$, in agreement with the statement of Ciamician and Silber.*

The oxidation therefore took place in accordance with the following reactions,



and the dichlorpyromucic acid in question is thus conclusively shown to have its chlorine atoms in the β and γ positions.

PREPARATION OF ISOMERIC DICHLORPYROMUCIC ACIDS.

Although we had been unable to find the $\beta\delta$ dichlorpyromucic acid among the products formed by the action of alkalies upon ethyl pyromucic tetrachloride, it seemed to us probable that it might be formed under the proper conditions by the direct action of chlorine upon ethyl pyromucate, or by the decomposition of its tetrachloride by heat alone.

Tönnies† had already shown that δ brompyromucic acid could be formed by heating pyromucic tetrabromide, and Hill and Sanger‡ had further shown that δ brompyromucic acid and $\beta\delta$ dibrompyromucic acid could conveniently be made by the action of bromine upon pyromucic acid at high temperature. As subsequent experiments in this laboratory had shown that these two acids could more advantageously be made by substituting the ethyl ether for the acid, and our own experiments had shown that the δ chlorpyromucic acid could readily be made in this way, we proceeded to study the action of chlorine upon ethyl pyromucate at high temperature. It seems hardly necessary to describe in detail the numerous experiments which we made under widely varying conditions, each one of which yielded us purely negative results. Ethyl pyromucate was treated with chlorine at

* Berichte d. deutsch. chem. Gesellsch., xvi. 2396.

† Ibid., xi. 1088.

‡ These Proceedings, xxi. 136, 160.

temperatures ranging from 145° to its boiling point, both by itself and after the addition of iodine or aluminic chloride, but in no case was the desired product obtained. Pyromucic acid and δ chlorpyromucic acid also failed to give such a product when treated at high temperatures with chlorine, and we were equally unsuccessful when we used the chloranhydrides of these acids either with or without an excess of phosphoric pentachloride. We then studied the action of heat upon the tetrachloride of pyromucic acid itself, of its chloranhydride and ethyl ether, and of the ethyl ether of δ chlorpyromucic acid, and found in each case that small quantities of a dichlorpyromucic acid were formed which closely resembled the $\beta\delta$ dibrompyromucic. A more careful investigation further proved that in the decomposition of the ethyl pyromucic tetrachloride a second new dichlorpyromucic acid was formed concerning whose constitution we are not yet able to speak definitely. This acid we propose to call the χ dichlorpyromucic acid until its structure is established. The amount of the dichlorpyromucic acids which we have been able to obtain is but small, and we have made many unsuccessful attempts to increase the yield by varying the temperature or the mode of heating, or by adding iodine, or aluminic or ferric chloride, before heating.

We first obtained the $\beta\delta$ dichlorpyromucic acid by distilling under ordinary pressure the product formed by treating pyromucic acid with chlorine at 100°. Hydrochloric acid is given off in quantity, and, although a large carbonaceous residue is left in the retort, a liquid distillate is obtained which, after repeated distillation through a Hempel's column, amounts to about 85 per cent of the weight of the pyromucic acid taken and then distills leaving but an insignificant carbonaceous residue. This distillate is extremely complex in its nature and we have as yet made no thorough study of its constituents. We found, however, that the portions which boiled between 196° and 220° gave considerable quantities of $\beta\delta$ dichlorpyromucic acid when treated with cold water. They therefore contained the corresponding chloranhydride of the acid. The yield thus obtained amounted to but about 4 per cent of the pyromucic acid taken. From ethyl pyromucic tetrachloride we succeeded in obtaining a somewhat better yield. We found it advantageous to purify the tetrachloride by one distillation *in vacuo*, and to distil the product thus obtained under ordinary pressure. More or less carbonization ensued, and on fractional distillation *in vacuo* through a Hempel's column * the distillate

* For fractional distillation under diminished pressure we used the extremely convenient apparatus of Anschütz. We found that the ease of separation could

was found to contain considerable unaltered tetrachloride. That portion which boiled above 140° under 16 mm. pressure was therefore redistilled under ordinary pressure and the distillate again fractionated *in vacuo*. After repeated distillations we found that the portion which boiled between 118° and 123° under 16 mm. pressure partially solidified on cooling, and that a few crystals were also formed in the next lower fraction. These fractions were therefore strongly cooled and the crystalline solid removed by filtration and the liquid portions further distilled. The solid thus obtained proved to be the ethyl ether of the new χ dichlorpyromucic acid melting at $197-198^{\circ}$, which we shall presently describe. When no more of this crystalline ether could be obtained by cooling, the liquid fractions were saponified by alcoholic sodic hydrate, the acids liberated by hydrochloric acid and separated through their calcium and barium salts. From the fraction boiling below 110° (16 mm.) we obtained chiefly δ chlorpyromucic acid melting at $176-177^{\circ}$, although it yielded also a small quantity of $\beta\delta$ dichlorpyromucic acid, which was readily isolated by means of its sparingly soluble barium salt. The fractions $110-118^{\circ}$ and $118-123^{\circ}$ apparently consisted chiefly of the ethyl ether of $\beta\delta$ dichlorpyromucic acid, but the latter necessarily contained also a small amount of the crystalline ethyl χ dichlorpyromucate held in solution. The two dichlorpyromucic acids could readily be separated through the different solubilities of their calcium salts, the calcic $\beta\delta$ dichlorpyromucate like the calcium salt of the corresponding bromine derivative being very sparingly soluble in water. From 123° to 130° but an insignificant fraction was collected and the fraction $130^{\circ}-153^{\circ}$ consisted in part at least of unaltered ethyl pyromucic tetrachloride, from which $\beta\gamma$ dichlorpyromucic acid was obtained.

100 grm. of ethyl pyromucate yielded us 197 grm. of the tetrachloride and from this we obtained the following weights of pure products:

be materially increased by filling a few inches of the stem of the distilling flask with glass beads, and thus combining the Hempel's column with the vacuum distillation. The beads were supported upon a perforated disk of platinum foil slipped over the capillary air tube and held in place by a slight enlargement of the tube. The thermometer was then raised to the proper line by a short bit of small glass tubing dropped into the air tube. Hantzsch (Ann. Chem. u. Pharm., ccxlix. 57) has used with advantage for distillation under ordinary pressure a long necked boiling flask whose stem is partially filled with beads supported upon a platinum foil forced into the neck. We have for a long time used such a Hempel's column, but have supported the beads conveniently upon a glass bulb which nearly fills the stem and whose sealed neck is long enough to rest upon the bottom of the flask.

- 5.0 gm. δ chlorpyromucic acid.
- 12.2 gm. $\beta\delta$ dichlorpyromucic acid.
- 2.7 gm. χ dichlorpyromucic acid.
- 16.1 gm. ethyl χ dichlorpyromucate.

If pyromucyl chloride is treated with chlorine at 0° , the chlorine is absorbed very slowly, but the gain in weight finally approximately corresponds with that required for the formation of a tetrachloride. If the tetrachloride is distilled under ordinary pressure, only an inconsiderable carbonaceous residue is left in the retort, and after repeated distillations through a Hempel's column under ordinary pressure a product is obtained which, when treated with water, yields the $\beta\delta$ dichlorpyromucic acid and the χ dichlorpyromucic acid. While the yield of the $\beta\delta$ dichlorpyromucic acid thus obtained is somewhat greater than that obtained from the ethyl pyromucic tetrachloride, the yield of the χ dichlorpyromucic acid is much smaller.

By treating ethyl δ chlorpyromucate in the cold with chlorine, and distilling the addition product thus formed under ordinary pressure, we also obtained the $\beta\delta$ dichlorpyromucic acid. While the yield was somewhat larger than that obtained from the ethyl pyromucic tetrachloride, it did not repay us for the loss of time and material involved in making the δ chlorpyromucic acid. Moreover, to our surprise, we could obtain in this way none of the crystalline ethyl χ dichlorpyromucate.

$\beta\delta$ DICHLORPYROMUCIC ACID.

The acid whose preparation has just been described can most readily be purified by repeated precipitation from ammoniacal solution with calcic chloride, and recrystallization from chloroform. The acid thus purified gave on analysis the following results:

- I. 0.2577 gm. substance gave 0.3129 gm. CO_2 and 0.0259 gm. H_2O .
- II. 0.1933 gm. substance gave 0.3053 gm. AgCl .

	Calculated for $\text{C}_6\text{H}_2\text{ClO}_5$.	Found.	
		I.	II.
C	33.15	33.11	
H	1.10	1.12	
Cl	39.22		39.04

$\beta\delta$ dichlorpyromucic acid is readily soluble in ether or alcohol. It dissolves readily in hot water, benzol, or chloroform, and the greater part of the acid is in each case deposited on cooling in oblique prisms, which are frequently twinned in forms which can hardly be distin-

guished from those of the $\beta\delta$ dibrompyromucic acid. The acid melts sharply at $155-156^\circ$, and sublimes unaltered at a higher temperature.

The solubility of the acid in water at $19^\circ.5$ was determined in the usual manner. A weighed quantity of a solution of the acid saturated at $19^\circ.5$ was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid:

- I. 42.8007 grm. solution saturated at $19^\circ.5$ gave 0.0724 grm. BaSO_4 .
 II. 51.4109 grm. solution saturated at $19^\circ.5$ gave 0.0907 grm. BaSO_4 .

According to these determinations, the solution saturated at $19^\circ.5$ contained the following percentages of acid:

I.	II.
0.26	0.27

Baric $\beta\delta$ Dichlorpyromucate, $\text{Ba}(\text{C}_6\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$. — The barium salt was prepared by precipitating a dilute solution of the ammonium salt with baric chloride, and recrystallizing the product thus obtained from water. The salt is sparingly soluble in hot water, still less soluble in cold water, and crystallizes from a hot concentrated solution in long irregular flat prisms which contain four molecules of water.

The salt is permanent in the air, effloresces over sulphuric acid, and loses its water readily at 100° .

- I. 1.4513 grm. air-dried salt lost at 100° 0.1795 grm. H_2O .
 II. 0.4908 grm. air-dried salt gave 0.1981 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_6\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.	I.	Found.	II.
H_2O	12.66	12.37		
Ba	24.07			23.73

0.4751 grm. salt dried at 100° gave 0.2205 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_6\text{HCl}_2\text{O}_3)_2$.	Found.
Ba	27.56	27.29

The solubility of the salt in water at 19.5° was determined in the usual manner.

- I. 28.4671 grm. solution saturated at $19^\circ.5$ gave 0.0561 grm. BaSO_4 .
 II. 28.6844 grm. solution saturated at $19^\circ.5$ gave 0.0573 grm. BaSO_4 .

The solution saturated at $19^\circ.5$ therefore contained the following percentages of anhydrous salt:

I.	II.
0.42	0.43

Calcic $\beta\delta$ Dichlorpyromucate, $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$. — The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride, and recrystallizing the product from hot water. It is but sparingly soluble in hot water, still less soluble in cold water, and separates from a hot concentrated solution in flattened prisms with rectangular terminations. The crystallized salt is permanent in the air, effloresces slowly over sulphuric acid and loses all its water at 125° .

I. 1.5490 grm. air-dried salt lost at 125° 0.1820 grm. H_2O .

II. 0.4067 grm. air-dried salt gave 0.1219 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 3 \text{H}_2\text{O}$.	I.	Found.	II.
H_2O	11.90	11.75		
Ca	8.81			8.81

0.6899 grm. salt dried at 125° gave 0.2332 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ca	10.00	9.94

The solubility of the salt in water at $19^\circ.5$ was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

I. 32.1733 grm. solution saturated at $19^\circ.5$ gave 0.0244 grm. CaSO_4 .

II. 36.7555 grm. solution saturated at $19^\circ.5$ gave 0.0289 grm. CaSO_4 .

The solution saturated at $19^\circ.5$ therefore contained the following percentages of anhydrous salt:

I.	II.
0.22	0.23

Ethyl $\beta\delta$ Dichlorpyromucate, $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$. — The ethyl ether was prepared by the action of ethyl iodide on the silver salt, and is a heavy liquid of pleasant odor. It melts at $2-3^\circ$ and distils at $116-118^\circ$ under a pressure of 16 mm., the oil bath being at $165-175^\circ$. An analysis of the distilled ether gave the following result.

0.2157 grm. substance gave 0.2957 grm. AgCl .

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$.	Found.
Cl	33.98	33.89

$\beta\delta$ Dichlorpyromucamide, $\text{C}_5\text{HCl}_2\text{O}_2\text{NH}_2$. — The ethyl ether is but slowly attacked by concentrated ammonia in the cold, but at 100° it is readily converted to the amide. The amide is sparingly soluble in

cold water, more readily in hot, and separates from a hot concentrated solution in long needles which on standing are converted into oblique prisms which melt at 153–154°.

0.2781 grm. substance dried over H_2SO_4 gave 20.0 c.c. moist N at 25.5° under a pressure of 766 m.m.

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_2\text{NH}_2$.	Found.
N	7.78	8.06

Although the melting point, the crystalline form, and the insolubility of its calcium salt showed that this acid closely resembled the $\beta\delta$ dibrompyromucic acid, it was evidently necessary to establish the position of the chlorine atoms by means of its oxidation products.

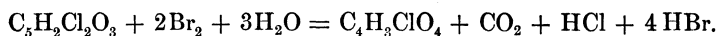
Action of Bromine and Water.

Hill and Sanger* found that the $\beta\delta$ dibrompyromucic acid was readily attacked by aqueous bromine in the cold with the formation of monobrommaleyl bromide. The $\beta\delta$ dichlorpyromucic acid is but slowly attacked by aqueous bromine in the cold, and we therefore suspended it in five times its weight of water, added at once somewhat more than four atoms of bromine, heated until the oil which was first formed had almost all disappeared, and evaporated the solution at a gentle heat. The crystalline mass thus obtained was readily soluble even in cold water, and very sparingly soluble even in hot chloroform or benzol. The product was dissolved in cold water, filtered, and evaporated nearly to dryness. The crystals which separated were pressed dry with filter paper, washed carefully with hot benzol, and recrystallized from a little hot water. The acid thus prepared crystallized in microscopic crystals, which melted at 189–190°,† and proved on analysis to contain the percentage of chlorine required by monochlorfumaric acid.

0.1288 grm. substance dried over H_2SO_4 gave 0.1227 grm. AgCl.

	Calculated for $\text{C}_4\text{H}_3\text{ClO}_4$.	Found.
Cl	23.59	23.55

The oxidation with bromine and water therefore takes place in accordance with the following equation :



* These Proceedings, xxi. 165.

† Kauder (Journal für prakt. Chemie, [2], xxxi. 28) gives the melting point as 191°.

Since the $\beta\delta$ dichlorpyromucic is but slowly attacked even by concentrated nitric acid, it was not thought worth while to study the reaction in detail.

χ DICHLORPYROMUCIC ACID.

The formation of the ethyl ether of this acid by the decomposition of ethyl pyromucic tetrachloride has already been described. The ether was recrystallized from hot alcohol, and saponified by alcoholic sodic hydrate. On the addition of hydrochloric acid to the aqueous solution of the sodium salt, a sparingly soluble acid separates, which may easily be purified by recrystallization from hot water.

The acid dried over sulphuric acid gave on analysis the following results:—

- I. 0.2196 grm. substance gave 0.2672 grm. CO_2 and 0.0237 grm. H_2O .
 II. 0.2212 grm. substance gave 0.3492 grm. AgCl .

	Calculated for $\text{C}_5\text{H}_2\text{Cl}_2\text{O}_3$	I.	Found.	II.
C	33.15	33.18		
H	1.10	1.20		
Cl	39.22			39.03

χ dichlorpyromucic acid is readily soluble in ether or alcohol, and but sparingly soluble in cold water. In hot water it is freely soluble, and crystallizes as the solution cools in long needles which melt at $197-198^\circ$. The acid readily sublimes unchanged below its melting point. Sodium amalgam slowly reduces it to pyromucic acid melting at $129-130^\circ$.

The solubility of the acid in water at $19^\circ.5$ was determined in the usual manner. A solution of the acid saturated at $19^\circ.5$ was boiled with baric carbonate, and the barium dissolved determined by precipitation with sulphuric acid.

- I. 38.2670 grm. solution saturated at $19^\circ.5$ gave 0.0322 grm. BaSO_4 .
 II. 37.5125 grm. solution saturated at $19^\circ.5$ gave 0.0301 grm. BaSO_4 .

The solution saturated at $19^\circ.5$ therefore contained the following percentages of acid:—

I.	II.
0.13	0.12

Baric χ Dichlorpyromucate, $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4 \text{H}_2\text{O}$.—The barium salt may most readily be prepared by boiling the acid with baric carbonate. The salt is quite readily soluble in cold water, more soluble in hot water, and crystallizes in columnar aggregations of prisms which

contain four molecules of water. The crystallized salt is stable in the air, effloresces over sulphuric acid, and loses all its water at 100° .

I. 1.0471 grm. air-dried salt lost at 100° 0.1285 grm. H_2O .

II. 0.5464 grm. air-dried salt gave 0.2235 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.	Found.	
		I.	II.
H_2O	12.66	12.27	
Ba	24.07		24.05

0.4495 grm. salt dried at 100° gave 0.2091 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ba	27.56	27.35

The solubility of the salt in water at $19^{\circ}.5$ was determined in the usual manner.

I. 11.1910 grm. solution saturated at $19^{\circ}.5$ gave 0.0820 grm. BaSO_4 .

II. 8.6544 grm. solution saturated at $19^{\circ}.5$ gave 0.0644 grm. BaSO_4 .

According to these determinations, the solution saturated at 20° contained the following percentages of anhydrous salt:—

I.	II.
1.56	1.59

Calcic χ Dichloropyromucate, $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$. — The calcium salt was prepared by boiling the acid with calcic carbonate. The filtered solution was then concentrated on the water bath to a small volume, and the salt which separated was filtered out and washed with a little water. Since the salt appeared to be about as soluble in cold water as in hot, it was dissolved in water and the solution concentrated *in vacuo* over sulphuric acid. The salt which separated was then pressed dry with filter paper. It is quite readily soluble in water, and crystallizes in prisms which contain four molecules of water. The crystallized salt is permanent in the air, effloresces slowly over sulphuric acid, and loses all its water at 117° .

I. 0.9075 grm. air-dried salt lost at 117° 0.1380 grm. H_2O .

II. 0.6080 grm. air-dried salt gave 0.1746 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$.	Found.	
		I.	II.
H_2O	15.25	15.21	
Ca	8.48		8.44

0.3377 grm. salt dried at 117° gave 0.1152 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{HCl}_2\text{O}_3)_2$.	Found.
Ca	10.00	10.02

The solubility of the salt in water at 19°.5 was determined in the usual manner. The calcium was precipitated as oxalate and ignited with sulphuric acid.

- I. 6.5743 grm. solution saturated at 19°.5 gave 0.1522 grm. CaSO_4 .
 II. 7.2115 grm. solution saturated at 19°.5 gave 0.1689 grm. CaSO_4 .

The solution saturated at 19°.5 therefore contained the following percentages of anhydrous salt:

I.	II.
6.81	6.89

Ethyl χ *Dichlorpyromucate*, $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$. — The process by which the ethyl ether was obtained has already been described. It is readily soluble in hot alcohol, sparingly soluble in cold alcohol, and crystallizes in clustered prisms with rectangular truncations which melt at 72–73°. A sample of the ether melting at 72–73° was distilled under a pressure of 16 mm. and boiled constant at 122°.5, temperature of bath 170–175°. For analysis the ether was dried over sulphuric acid.

- I. 0.2034 grm. substance gave 0.2790 grm. AgCl .
 II. 0.2302 grm. substance gave 0.3160 grm. AgCl .

	Calculated for $\text{C}_5\text{HCl}_2\text{O}_3\text{C}_2\text{H}_5$.	Found.	
		I.	II.
Cl	33.98	33.91	33.94

In order to determine the constitution of this dichlorpyromucic acid we studied its oxidation products with aqueous bromine.

Action of Bromine and Water.

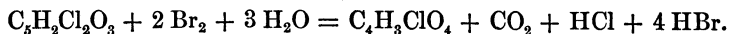
As it was desirable to compare the oxidation product obtained from this acid with that obtained from the $\beta\delta$ dichlorpyromucic acid under the same conditions, the acid was suspended in five times its weight of water, somewhat more than four atoms of bromine added as rapidly as possible, and the solution boiled until the oil which was at first formed had nearly disappeared. The filtered solution was evaporated to dryness at a gentle heat, the crystalline residue dissolved in a little cold water, filtered, and again evaporated nearly to dryness. The acid which separated was readily soluble even in cold water, almost insoluble in hot chloroform or benzol. It was therefore pressed dry with filter paper and carefully extracted with hot benzol. The acid as thus prepared crystallized in microscopic crystals which melted at 188–189°, and moreover gave on analysis the percentage of chlorine required by monochlorfumalic acid.*

* Kauder, *loc. cit.*

0.1441 grm. substance dried over H_2SO_4 gave 0.1377 grm. AgCl .

	Calculated for $\text{C}_4\text{H}_3\text{ClO}_4$.	Found.
Cl	23.59	23.62

The χ dichlorpyromucic acid, like the $\beta\delta$ dichlorpyromucic acid, therefore gives with aqueous bromine as the chief product chlorfumaric acid according to the equation



Since the oxidation with bromine had shown with sufficient precision that one of the chlorine atoms of the χ dichlorpyromucic acid occupied the δ position, we thought it unnecessary for our purposes to study also the action of nitric acid.

Action of Fuming Sulphuric Acid.

The two isomeric dibrompyromucic acids had shown marked differences in their behavior toward fuming sulphuric acid.* While the $\beta\gamma$ acid had rapidly been converted into the corresponding sulphonic acid, brommaleic acid in nearly theoretical quantity had been formed from the $\beta\delta$ dibrompyromucic acid, and no trace of a sulphonic acid could be detected. Preliminary experiments proved that the $\beta\gamma$ and $\beta\delta$ dichlorpyromucic acids showed a similar difference in their behavior toward fuming sulphuric acid. While the formation of chlormaleic acid in the latter case could not definitely be proved, certainly no sulphonic had been formed, and it seemed to us of interest to study also the behavior of the third isomeric dichlorpyromucic acid under the same conditions. χ dichlorpyromucic acid dissolves readily in fuming sulphuric acid, and if care be taken to prevent any marked elevation of temperature no very essential decomposition ensues, although a slight effervescence is noticeable. After the solution of the acid in four times its weight of fuming sulphuric acid had stood for thirty-six hours, it was poured into a large amount of cold water, the solution cooled, and thoroughly extracted with ether. The ethereal extract left on evaporation a small quantity of a colorless oil which reduced silver oxide, and whose vapor vigorously attacked the eyes and nose. The amount of oil thus obtained was wholly insufficient for further study. On standing, it deposited a few clustered needles, which probably were unaltered acid, although they may possibly have been the decomposition product subsequently described. From the aqueous solution the barium salt was prepared in the usual way, and,

* These Proceedings, xxiii. 218.

since the properties of the neutral salt were unfavorable to purification, it was converted into the acid salt, and this recrystallized from hot water. The acid salt was readily soluble in hot water, more sparingly soluble in cold water and crystallized in triclinic (?) prisms which effloresced on exposure to the air. It gave an excellent qualitative reaction for sulphur, and when dried over sulphuric acid* gave the percentage of barium required by the formula $\text{Ba}(\text{C}_5\text{HCl}_2\text{SO}_6)_2$.

0.3886 grm. of the salt dried over sulphuric acid gave 0.1338 grm.

BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{HCl}_2\text{SO}_6)_2$	Found.
Ba	20.84	20.24

Baric χ *Dichlorsulphopyromucate*, $\text{BaC}_5\text{Cl}_2\text{SO}_6 \cdot 2 \text{H}_2\text{O}$. — From the acid barium salt we prepared the neutral salt by neutralizing its aqueous solution with baric carbonate. Since the hot saturated solution deposited little or nothing on cooling, it was evaporated *in vacuo* over sulphuric acid. The salt then crystallized in sheaves of prisms which appeared to be triclinic. It was permanent in the air, effloresced over sulphuric acid, and lost its water completely at 160° .

1.4159 grm. of the air-dried salt lost at 160° 0.1277 grm. H_2O .

	Calculated for $\text{BaC}_5\text{Cl}_2\text{SO}_6 \cdot 2 \text{H}_2\text{O}$	Found.
H_2O	8.33	9.02

0.5296 grm. of the salt dried at 160° gave 0.3126 grm. BaSO_4 .

	Calculated for $\text{BaC}_5\text{Cl}_2\text{SO}_6$	Found.
Ba	34.59	34.69

The formation of a dichlorsulphopyromucic acid by the action of fuming sulphuric acid upon the χ dichlorpyromucic acid is thus sufficiently established. The bromsulphopyromucic acids are so readily reduced in alkaline solution that we hoped to be able to prepare from this dichlorsulphopyromucic acid the corresponding sulphopyromucic acid, and thus establish the position of the two chlorine atoms. We soon found, however, that the chlorine was held with unusual persistence, and with the material at our disposal we have as yet been unable to reach decisive results.

* The single determination of the water of crystallization was unfortunately defective. It gave 13.34 per cent of water in the salt dried by short exposure to the air, while a salt crystallizing with $2\frac{1}{2}$ molecules of water should contain 13.70 per cent.

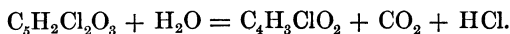
Decomposition by Hydrochloric Acid.

If the χ dichlorpyromucic acid is heated with water in a sealed tube to 170° , no change is effected, but a reaction which we had in no way anticipated takes place if it is heated upon the water bath in an open flask with concentrated hydrochloric acid. Carbonic acid is evolved, and in a short time the acid is completely decomposed with the formation of a neutral body which volatilizes when the solution is boiled, and which can be extracted, although with difficulty, from the distillate, or from the original solution with ether. The ethereal solution left on evaporation a white crystalline solid which was sparingly soluble in water, readily soluble in cold chloroform or benzol, and but sparingly soluble in ligroin. When recrystallized from ligroin it formed long slender lustrous prisms, which melted at $52\text{--}53^\circ$, and sublimed rapidly at ordinary temperatures. It reduced argentic oxide on warming, and dissolved in aqueous alkalies, forming a yellow solution. The physical properties and the behavior of this substance at once recalled to our minds the crystalline body melting at 77° which Hill and Sanger* had obtained in small quantity from the by-products of the decomposition of pyromucic tetrabromide by alcoholic sodic hydrate. The formula of this body had been shown to be $\text{C}_4\text{H}_3\text{BrO}_2$ and an analysis of the new substance left no doubt of its similar composition.

0.1045 grm. substance gave 0.1261 grm. AgCl .

	Calculated for	Found.
	$\text{C}_4\text{H}_3\text{ClO}_2$.	
Cl	29.95	29.84

This interesting body is probably formed according to the reaction



And since we found little difficulty in obtaining 40 per cent of the yield which this equation demands, it will be possible to study it more in detail. Unfortunately, it was discovered so late in our work as to make it impossible to present the results of such a study in this paper. While it would be easy for us to venture a conjecture as to its structure, we prefer to await the results of a future investigation.

TRICHLORPYROMUCIC ACID.

For the preparation of the trichlorpyromucic acid it was evidently most convenient to decompose with alkalies the tetrachloride of the δ chlorpyromucic acid. It did not seem necessary, however, to pre-

* These Proceedings, xxi. 158.

pare this tetrachloride in a pure condition, and indeed we first obtained the trichlorpyromucic acid from one of the earlier preparations of the ethyl pyromucic tetrachloride in which an unusually great spontaneous elevation of temperature had taken place through the rapid absorption of chlorine. For its preparation we heated the ethyl pyromucate to 145° , and passed in chlorine at this temperature until the gain in weight showed that one atom of hydrogen had been replaced by chlorine. We then allowed the temperature to fall to about 120° , and continued the chlorination to saturation. The total gain in weight then corresponded approximately to that required by the formation of the tetrachloride of the ethyl chlorpyromucate. On decomposing this product as usual with a cold concentrated alcoholic solution of sodic hydrate, the alcoholic solution filtered from the insoluble sodium salts contained, as in the previous cases, small quantities of liquid furfuran derivatives, but the amount was so minute that no separate study of them was made. The sodium salts dissolved in hot water gave with hydrochloric acid an impure trichlorpyromucic acid as a more or less colored oil, which solidified as the solution cooled. For the purification of the acid we have found it convenient to take advantage of the slight solubility of the ammonium salt in cold water. The crude acid was suspended in about thirty times its weight of water, ammoniac hydrate added in excess, and the hot solution treated with bone-black. The filtered solution deposits on cooling the greater part of the trichlorpyromucic acid as the ammonium salt from which the pure acid can readily be obtained. The small amount of trichlorpyromucic acid remaining in the ammoniacal solution may be recovered, although at the expense of considerable trouble, by precipitation with calcic chloride and repeated recrystallization from water and dilute alcohol of the acid obtained from the insoluble calcium salt.

The yield of pure trichlorpyromucic acid was far from satisfactory, as we could obtain only 30 per cent of the weight of the ethyl pyromucate taken, but 15 per cent of the theoretical amount.

For analysis the acid was dried over sulphuric acid.

- I. 0.3214 grm. substance gave 0.3248 grm. CO_2 and 0.0211 grm. H_2O .
- II. 0.2107 grm. substance gave 0.4192 grm. AgCl .
- III. 0.2135 grm. substance gave 0.4255 grm. AgCl .

	Calculated for $\text{C}_5\text{HCl}_3\text{O}_3$	I.	Found II.	III.
C	27.85	27.56		
H	0.46	0.73		
Cl	49.43		49.19	49.27

Trichlorpyromucic acid is readily soluble in alcohol or ether, quite readily soluble in boiling benzol, and but sparingly soluble in cold benzol. Hot water dissolves it but sparingly, and as the solution cools most of the acid is deposited in microscopic needles which melt at 172–173°. This melting point was so much below that which we had been led to expect from analogy to the known acid containing bromine that we felt some doubt of its correctness, more especially since the crude acid was so far from pure. A sample of the acid melting at 172–173° was therefore recrystallized twice from water and then three times from benzol without perceptibly changing the melting point. The acid was then converted into the calcium salt, and this separated by crystallization into three successive fractions. The acid from these three fractions melted simultaneously and sharply at 172–173°. Finally, the ethyl ether was made, and the acid prepared from the repeatedly recrystallized pure ether melted at the same point.

The solubility of the acid in water at 19°.5 was determined by boiling with baric carbonate a weighed quantity of a solution of the acid saturated at that temperature, and determining the barium dissolved as sulphate.

I. 49.1742 grm. solution saturated at 19°.5 gave 0.0344 grm. BaSO_4 .

II. 47.0228 grm. solution saturated at 19°.5 gave 0.0331 grm. BaSO_4 .

The solution saturated at 19.5° therefore contained the following percentages of acid :

I.	II.
0.13	0.13

Baric Trichlorpyromucate, $\text{Ba}(\text{C}_5\text{Cl}_3\text{O}_8)_2 \cdot 4 \text{H}_2\text{O}$. — The barium salt was prepared by precipitating a dilute solution of the ammonium salt with baric chloride, and recrystallizing the sparingly soluble salt thus thrown down from hot water. The salt proved to be but sparingly soluble even in hot water, and still less soluble in cold water. It separates from a hot concentrated solution in needles which apparently contain four molecules of water. The salt is permanent in the air, but loses three molecules of its crystal water over sulphuric acid. When dried at 120°, it still retains a half-molecule of water which cannot be expelled without essential decomposition.

I. 0.6847 grm. air-dried salt gave 0.2511 grm. BaSO_4 .

II. 0.6205 grm. air-dried salt gave 0.2273 grm. BaSO_4 .

III. 0.5672 grm. air-dried salt gave 0.2076 grm. BaSO_4 .

IV. 1.3625 grm. air-dried salt lost over H_2SO_4 0.1148 grm. H_2O and at 120° 0.1338 grm. H_2O .

V. 1.1645 grm. air-dried salt lost over H_2SO_4 0.1003 grm. H_2O and at 100° 0.1124 grm. H_2O .

VI. 1.3000 grm. air-dried salt lost over H_2SO_4 0.1124 grm. H_2O and at 100° 0.1256 grm. H_2O .

	Calculated for $\text{Ba}(\text{C}_5\text{Cl}_3\text{O}_3)_2 \cdot 4 \text{H}_2\text{O}$.	I.	II.	Found. III.	IV.	V.	VI.
Ba	21.47	21.56	21.54	21.52			
3 H_2O	8.46				8.43	8.61	8.65
$3\frac{1}{2}$ H_2O	9.87				9.83	9.65	9.66

I. 0.7484 grm. substance dried at 120° gave 0.3038 grm. BaSO_4 .

II. 0.6247 grm. substance dried at 100° gave 0.2521 grm. BaSO_4 .

III. 0.6497 grm. substance dried at 100° gave 0.2634 grm. BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_5\text{Cl}_3\text{O}_3)_2 \cdot \frac{1}{2} \text{H}_2\text{O}$.	I.	Found. II.	III.
Ba	23.83	23.86	23.72	23.84

The solubility of the salt in water at $19^\circ.5$ was determined in the usual way.

I. 41.4499 grm. solution saturated at $19^\circ.5$ gave 0.0470 grm. BaSO_4 .

II. 44.9822 grm. solution saturated at $19^\circ.5$ gave 0.0500 grm. BaSO_4 .

The solution saturated at $19^\circ.5$ therefore contained the following percentages of anhydrous salt : —

I.	II.
0.27	0.27

Calcic Trichloropyromucate, $\text{Ca}(\text{C}_5\text{Cl}_3\text{O}_3)_2 \cdot 4 \text{H}_2\text{O}$. — The calcium salt was prepared by precipitating a dilute solution of the ammonium salt with calcic chloride. The precipitated salt was then crystallized from hot water, and proved to be sparingly soluble in hot water, still less soluble in cold water, and separated from a hot solution in irregular aggregations of small leafy plates.

The salt is permanent in the air, effloresces over sulphuric acid, and loses all its water at 110° .

I. 1.3008 grm. air-dried salt lost at 110° 0.1697 grm. H_2O .

II. 1.8389 grm. air-dried salt lost at 110° 0.2417 grm. H_2O .

	Calculated for $(\text{C}_5\text{Cl}_3\text{O}_3)_2\text{Ca} \cdot 4 \text{H}_2\text{O}$.	I.	Found. II.
H_2O	13.30	13.05	13.14

I. 0.6399 grm. salt dried at 110° gave 0.1855 grm. CaSO_4 .

II. 0.6974 grm. salt dried at 110° gave 0.2019 grm. CaSO_4 .

	Calculated for $\text{Ca}(\text{C}_5\text{Cl}_3\text{O}_3)_2$.	I.	Found. II.
Ca	8.53	8.53	8.51

The solubility of the salt in water at $19^{\circ}.5$ was determined in the usual manner. The calcium was precipitated as oxalate, and the oxalate ignited with sulphuric acid.

- I. 18.1457 grm. solution saturated at $19^{\circ}.5$ gave 0.0342 grm. CaSO_4 .
 II. 14.6806 grm. solution saturated at $19^{\circ}.5$ gave 0.0265 grm. CaSO_4 .

The solution saturated at $19^{\circ}.5$ therefore contained the following percentages of anhydrous salt:—

I.	II.
0.65	0.62

Potassic Trichloropyromucate, $\text{KC}_5\text{Cl}_3\text{O}_3$.—The potassium salt was prepared by boiling the acid with a slight excess of potassic carbonate. The solution was then concentrated until the salt began to separate, and on cooling it solidified to a mass of crystals, which were filtered off on the pump and pressed dry with filter paper. The salt is readily soluble even in cold water, and separates from a hot concentrated solution in sheaves of fine needles, which lose nothing in weight when heated to 120° . Analyses of the salt dried at this temperature proved it to be anhydrous.

- I. 0.5338 grm. salt dried at 120° gave 0.1851 grm. K_2SO_4 .
 II. 4425 grm. salt dried at 120° gave 0.1532 grm. K_2SO_4 .

	Calculated for $\text{KC}_5\text{Cl}_3\text{O}_3$.	Found.	
		I.	II.
K	15.42	15.57	15.54

Argentie Trichloropyromucate, $\text{AgC}_5\text{Cl}_3\text{O}_3$.—The silver salt may best be prepared by precipitating a hot solution of the calcium salt with argentic nitrate. For analysis the precipitated salt was well washed, and then recrystallized from hot water. It is sparingly soluble even in hot water, less soluble in cold water, and crystallizes from a hot concentrated solution in moss-like aggregations of fine needles.

The air-dried salt gave on analysis much too low a percentage of silver, and although the sample analyzed was free from calcium salt and free acid, it failed to give perfectly satisfactory results even when dried *in vacuo* over sulphuric acid or at 100° .

- I. 0.5142 grm. salt dried *in vacuo* over H_2SO_4 gave 0.2254 grm. AgCl .
 II. 0.4545 grm. salt dried at 100° gave 0.1998 grm. AgCl .

	Calculated for $\text{C}_5\text{Cl}_3\text{O}_3\text{Ag}$.	Found.	
		I.	II.
Ag	33.48	33.00	33.10

Ethyl Trichlorpyromucate, $C_5Cl_3O_3C_2H_5$. — The ethyl ether was prepared in the usual manner, by warming an alcoholic solution of the acid with concentrated sulphuric acid. 5 parts of the acid, 10 parts of absolute alcohol, and 5 parts of concentrated sulphuric acid (Sp. Gr. 1.84) were heated together for three hours at 100° . The ether was then precipitated with water, washed with warm dilute sodic carbonate, and finally with water. The ether is readily soluble in hot alcohol, more sparingly in cold alcohol, and crystallizes in flat prisms which melt at $62-63^\circ$.

- I. 0.2142 grm. substance dried over H_2SO_4 gave 0.3793 grm. AgCl.
 II. 0.2536 grm. substance dried over H_2SO_4 gave 0.4476 grm. AgCl.

	Calculated for $C_5Cl_3O_3C_2H_5$.	I.	Found.
			II.
Cl	43.74	43.77	43.64

Trichlorpyromucamide, $C_5Cl_3O_2NH_2$. — Concentrated aqueous ammonia attacks the trichlorpyromucic ether but slightly at ordinary temperatures. Even after three hours' heating in a sealed tube at 100° most of the ether was found to be unaltered, and we were obliged to prepare the amide from the acid chloride by the action of solid ammoniac carbonate. The amide is but sparingly soluble even in hot water and crystallizes in long slender needles, which melt at $160-161^\circ$.

0.3804 grm. substance dried over H_2SO_4 gave 23.2 c.c. moist N at 21° under a pressure of 765 mm.

	Calculated for $C_5Cl_3O_2NH_2$.	Found.
N	6.53	6.95

Although there could be no doubt as to the constitution of the trichlorpyromucic acid it seemed better for the sake of completeness to study its behavior with oxidizing agents.

Action of Bromine and Water.

Trichlorpyromucic acid was suspended in ten times its weight of cold water, and a little more than one molecule of bromine was added. Carbonic dioxide was evolved and the color of the bromine rapidly disappeared. When the reaction had been completed, a white insoluble substance remained, which was removed by filtration and washed with a dilute solution of sodic carbonate. The alkaline solution gave on acidification a copious precipitate of unaltered trichlorpyromucic acid, whose identity was established by the melting point $172-173^\circ$. The substance which remained undissolved by the alkaline solution

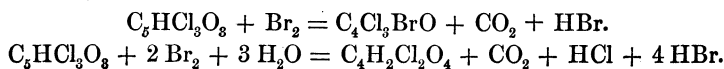
had the characteristic odor of the tetrabromfurfuran, and crystallized from hot alcohol in irregular plates, which melted at 75–76°. Analysis showed this substance to be a trichlorbromfurfuran.

- I. 0.1749 grm. substance dried over H_2SO_4 gave 0.4269 grm. AgCl and AgBr.
 II. 0.1411 grm. substance dried over H_2SO_4 gave 0.3447 grm. AgCl and AgBr.

	Calculated for $\text{C}_4\text{Cl}_3\text{BrO}$.	Found.	
		I.	II.
$\text{Cl}_3 + \text{Br}$	74.45	73.60	73.67

The strongly acid filtrate from the trichlorbromfurfuran and unaltered trichlorpyromucic acid yielded on extraction with ether a crystalline acid which was readily soluble in water. The amount of this acid was too small for analysis, but it was easily identified as dichlor-maleic acid by the melting point of its anhydride, 119–120°.*

The reaction had therefore taken place in accordance with the following equations:



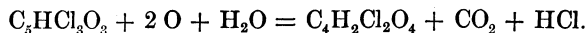
Action of Nitric Acid.

Trichlorpyromucic acid is but slowly attacked by nitric acid, and prolonged heating with moderately strong nitric acid is needed for complete oxidation. Even after heating the acid for six hours with six times its weight of nitric acid (Sp. Gr. 1.42) diluted with an equal weight of water, a portion of the trichlorpyromucic acid escaped oxidation. Carbonic dioxide was slowly given off, and a small quantity of an insoluble oil was formed, which had a peculiar penetrating odor not unlike that of substituted furfuran derivatives. Its quantity was too small to admit of its identification. In solution we were able to find nothing but dichlormaleic acid, which we purified through the barium salt and identified by the melting point of its anhydride and by analysis.

0.1997 grm. substance dried over H_2SO_4 gave 0.3086 grm. AgCl.

	Calculated for $\text{C}_4\text{H}_2\text{Cl}_2\text{O}_4$.	Found.
Cl	38.38	38.20

The reaction had therefore taken place in accordance with the following equation:



* Ciamician and Silber, *loc. cit.*

We have also prepared several other trisubstituted pyromucic acids, which may conveniently be described here.

βγ-DICHLOR-*δ*-BROMPYROMUCIC ACID.

Hill and Sanger* found that *βγ* dibrompyromucic acid was easily converted into tribrompyromucic acid by the action of bromine at ordinary temperatures.

If *βγ* dichlorpyromucic acid is exposed to the vapors of bromine at ordinary temperatures, bromine is rapidly absorbed, hydrobromic acid is evolved, and the gain in weight approaches that required by the displacement of hydrogen by bromine. The product was treated with small quantities of boiling water to remove unaltered dichlorpyromucic acid, and then recrystallized from dilute alcohol, and finally from water. The acid is readily soluble in alcohol or ether, dissolves freely in boiling benzol, more sparingly in cold benzol. Even in boiling water it is very sparingly soluble. It crystallizes in short clustered prisms, which melt at 185–186°.

0.3189 gm. substance dried over H₂SO₄ gave 0.5817 gm. AgCl and AgBr.

	Calculated for C ₆ HCl ₂ BrO ₃ .	Found.
Cl ₂ + Br	58.08	57.99

βγ-DIBROM-*δ*-CHLORPYROMUCIC ACID.

This acid we made by treating the ethyl *βγ* dibrompyromucate with chlorine and decomposing the product with alcoholic sodic hydrate. On acidifying the aqueous solution of the sodium salts thus obtained, a crystalline acid was precipitated, which after one recrystallization from dilute alcohol melted at 192–193°. After recrystallization from benzol the melting point rose to 193–194°. The acid was readily soluble in alcohol, ether, or hot benzol; sparingly soluble in cold benzol, or even in boiling water.

0.2315 gm. substance dried over H₂SO₄ gave 0.3960 gm. AgCl and AgBr.

	Calculated for C ₆ HClBr ₂ O ₃ .	Found.
Cl + Br ₂	64.19	64.37

We have attempted to prepare these acids also by the decomposition with alcoholic sodic hydrate of products formed by the addition of

* These Proceedings, xxi. 172.

bromine to δ chlorpyromucic acid and of chlorine to ethyl δ brompyromucate. Although we readily prepared in this way trisubstituted acids, the products in neither case were homogeneous, tribrom- or trichlorpyromucic acids being formed together with the acid containing both halogens.

$\beta\gamma$ -DICHLOR- δ -NITROPYROMUCIC ACID.

Hill and Palmer* have shown that $\beta\gamma$ dibrompyromucic acid is easily converted into a sulphonic acid by means of sulphuric acid, and that the sulpho group in this acid may readily be replaced by the nitro group. $\beta\gamma$ dichlorpyromucic acid was dissolved in fuming sulphuric acid, and the barium salt of the sulphonic acid isolated in the usual way. Since a more complete study of the salt did not fall within the plan of our work, we precipitated the barium exactly with sulphuric acid, and evaporated the dilute solution of the acid first at 100° and afterwards *in vacuo* over sulphuric acid. The crystalline somewhat deliquescent acid thus obtained was dissolved in several times its weight of fuming nitric acid, to which half its volume of concentrated sulphuric acid had been added. After the action was finished, the nitric acid was partially expelled, the residue diluted with water, and extracted with ether. The ether was then shaken with a dilute solution of sodic carbonate, and the acid precipitated from this alkaline solution by the addition of hydrochloric acid. The ethereal solution proved to contain no substance which invited further investigation.

The $\beta\gamma$ -dichlor- δ -nitropyromucic acid is readily soluble in alcohol, ether, or hot benzol. Hot water dissolves it freely, and on cooling the greater part of the acid is deposited in flattened leafy prisms which melt at 189 – 190° .

0.2168 grm. substance dried over H_2SO_4 gave 0.2756 grm. Ag. Cl.

	Calculated for $C_6HCl_2NO_5$.	Found.
Cl	31.42	31.42

We have as yet made no further study of this acid.

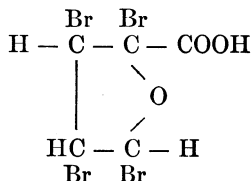
THEORETICAL CONSIDERATIONS.

The acids melting at 168 – 169° and 155 – 156° , which in the preceding pages we have called the $\beta\gamma$ and $\beta\delta$ dichlorpyromucic acids, are without doubt identical in structure with the two dibrompyromucic acids described by Hill and Sanger.† Their physical properties and

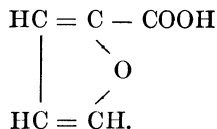
* These Proceedings, xxiii. 201, 205.

† These Proceedings, xxi. 137.

the solubility of their salts show their close relationship to these bromine derivatives, while the products formed from them by oxidation conclusively prove that they are structurally isomeric, and that the chlorine atoms occupy the same relative position that the bromine atoms hold in the dibrompyromucic acids. On reduction these two acids both yield the same chlorpyromucic acid, which in its turn closely resembles the β brompyromucic acid in its physical properties, although its melting point, 145–146°, is comparatively high. It is to be noted, however, that the $\beta\gamma$ dichlorpyromucic acid alone is formed by the action of alkalis upon the ethyl pyromucic tetrachloride, while the two isomeric dibrompyromucic acids are simultaneously formed under similar conditions. This simultaneous formation of the two structurally isomeric acids from pyromucic tetrabromide to which the formula



may be assigned led Hill and Sanger* to the conclusion that these acids must have their bromine atoms in the $\beta\gamma$ and $\beta\delta$ positions respectively, and that pyromucic acid itself probably had the formula



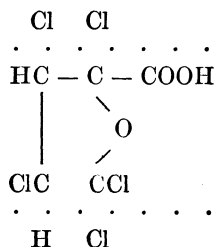
The structure of the $\beta\gamma$ and $\beta\delta$ dichlorpyromucic acids seems to us to be thus sufficiently established.

As to the third isomeric form, which for the present we have called the χ dichlorpyromucic acid, since it gives chlorfumaric acid by oxidation, it is evident that it must either have its chlorine atoms in the γ and δ position, or that it must be a geometrically isomeric form of the $\beta\delta$ acid. Unfortunately, we have been able to obtain as yet no evidence which conclusively proves either view to be correct. A dichlorpyromucic acid having its chlorine atoms in the γ and δ positions could not well be formed from ethyl pyromucic tetrachloride by the simple loss of hydrochloric acid. Tönnies† had shown that δ brom-

* These Proceedings, xxi. 182.

† Berichte de deutsch. chem. Gesellsch.

pyromucic acid could be formed by the action of heat upon pyromucic tetrabromide, when bromine must be eliminated as well as hydrobromic acid. Since we had noticed that hydrochloric acid invariably was evolved in the preparation of ethyl pyromucic tetrachloride, it seemed to us not improbable that the χ dichlorpyromucic acid was in fact the $\gamma\delta$ acid which had been formed in a similar way from the tetrachloride of the δ chlorpyromucic ether necessarily contained in the crude product.



We found, however, that no χ dichlorpyromucic acid was formed on heating ethyl δ chlorpyromucic tetrachloride, and that our product in this case contained the $\beta\delta$ acid alone, so that the molecule of chlorine, which had been eliminated in the reaction, had taken its chlorine atoms from the γ and δ positions. We hoped also to get further evidence as to the structure of the χ dichlorpyromucic acid by reducing it to a chlorpyromucic acid, or by substituting the chlorine of the χ dichlorpyromucic acid by hydrogen; but in neither case have we yet succeeded in obtaining well characterized products.

While it seems to us probable that the χ dichlor pyromucic acid is geometrically isomeric with the $\beta\delta$ acid, we have as yet been unable to convert one acid into the other. Both acids volatilize unchanged when heated, and the ordinary reagents which usually effect conversion in such cases have failed to bring about any perceptible isomerization. While lack of material has to a great degree limited our work with the χ acid, we have studied the behavior of the $\beta\delta$ acid under a variety of conditions with purely negative results. If the two acids are in fact geometrically isomeric, the simultaneous appearance of both forms in the distillation of ethyl pyromucic tetrachloride with the escape of large quantities of hydrochloric acid shows that the conversion of one acid into the other is effected with difficulty, while the formation of the $\beta\delta$ acid alone from the ethyl δ chlorpyromucic tetrachloride under similar conditions is especially worthy of note. Since pyromucic acid apparently contained two pairs of carbon atoms doubly

tied, the existence of geometrically isomeric forms of its derivatives seemed at the outset more than probable, and during the progress of the investigations which for many years have been carried on in this laboratory careful search had been made for such bodies, but hitherto only the two isomeric dibromfurfuran tetrabromides of Hill and Harts-horn* had been discovered. Since the discovery of the χ dichloropyromucic acid, which we made toward the close of our work, we have attempted to prepare the corresponding bromine derivative, but as yet without success. The isolation of the body $C_4H_3BrO_2$, which Hill and Sanger† found among the products of the decomposition of pyromucic tetrabromide by alkalis, certainly is an indication of the previous existence of such an acid, although it is by no means clear in what stage of the process the decomposition of the acid was effected, nor how the decomposition product itself escaped further alteration. Any detailed consideration of the geometrical structure of pyromucic acid we feel obliged to postpone until more facts bearing upon the question are at our disposal.

II.—ON CERTAIN DERIVATIVES OF FURFUR-ACRYLIC ACID.

By H. B. GIBSON AND C. F. KAHNWEILER.

Presented May 28, 1889.

THE preparation of furfuracrylic acid was described by v. Baeyer‡ 1877. At that time, however, the investigation of the acid was pushed in but one direction, and the successive steps by which it could be converted into a pimelic acid were alone described in detail. It seemed that a further study of the acid in other directions also could hardly fail to yield interesting results.

The ready decomposition of furfuracrylic acid by mineral acids compelled us to relinquish the line of work we originally had proposed to follow, and we consequently began an investigation into the nature of this decomposition. The study of the action of hydrochloric acid upon an alcoholic solution of furfuracrylic acid was just beginning

* Berichte der deutsch. chem. Gesellsch., xviii. 450.

† These Proceedings, xxi. 158.

‡ Ber. d. deutsch. chem. Gesellsch., x. 355.